<u>REMARKS</u>

Entry of the preceding amendment in response to the Office Action of March 31, 2008 on the above-identified application, and a reconsideration of the claims as amended, are respectfully requested.

Claims 1 and 3 through 6 are pending in the application. In the action, all claims were rejected on both formal and prior art grounds.

At the outset, in the preceding amendment claims 1 and 3 through 6 have generally been amended into the form taken by the claims in European Patent No. 1 497 477, which was granted on February 28, 2007 on European Patent Application No. 03717459.6. This European patent application corresponds to the present application; that is to say, more exactly, the applications are both national stage applications based on International Application No. PCT/IB2003/001555. A copy of European Patent No. 1 497 477 will be found enclosed for the convenience of the Examiner. Entry of the preceding amendment, in which cosmetic changes have been made to the claims of the European patent to place them into a form more in accord with the requirements of U.S. practice, is respectfully requested.

Referring to page 2 of the action, claims 1 and 3 through 6 were rejected under 35 U.S.C. § 112, first paragraph, as failing to comply with the written description requirement. The Examiner's reasoning was that the limitation that the film contains no fluorine, added to the claims in a previous amendment, was not supported by the specification and was believed to constitute new matter. The Examiner will note that this limitation has been removed in the amendment set forth above.

Further, referring to page 3 of the action, claims 1 and 3 through 6 were rejected under 35 U.S.C. § 103(a) as being unpatentable for obviousness over the teachings of U.S. Patent

No. 6,074,981 to Tada et al.

The Tada reference discloses that fluorine contained within a photocatalyst layer containing titanium oxide and other metallic oxide semiconductors increases the metallic oxides photocatalytic activity. According to the Tada reference, when using a base material that has an alkaline-containing glass composition, a fluorine-containing layer, such as a layer of fluorine containing silicon dioxide and other metallic oxide, between the photocatalyst film and the base material can prevent the deterioration of the photocatalytic activity of the photocatalyst layer. The fluorine-containing layer functions as an alkaline barrier that controls the diffusion and migration of alkali metallic ions in the glass fibers, such as sodium ions, into the photocatalyst layer, where they adversely affect its photocatalytic activity.

The Applicants believe that the Tada reference neither shows nor suggests the inventions as claimed in the preceding amendment, and comment as follows to the remarks made by the Examiner on pages 3 and 4 of the action:

1. <u>Tada</u>, column 2, line 59 to column 3, line 4

The Examiner has taken the position that the Tada reference teaches a photocatalyst layer preferably comprising titanium oxide, stating that the layer can be formed by vapor deposition, and that materials having various valence states are presented.

There are roughly two types of vacuum vapor deposition methods: the chemical vapor deposition and the physical vapor deposition. In the present invention, the sputtering process used in a type of physical vapor deposition. The physical vapor deposition may be done in other ways than by sputtering. It is publicly known, however, that crystalline films cannot be applied by sputtering, but can be applied by chemical vapor deposition. Later in the Tada specification,

the use of chemical vapor deposition is clearly mentioned in column 3, line 19, through 23, which leads one to conclude that Tada et al. adopted chemical vapor deposition, not sputtering. Moreover, the examples mentioned in the Tada reference and noted by the Examiner are various types of metal oxides, not degrees of oxidation in titanium metal oxides. Only the tetravalent titanium oxide is mentioned.

2. <u>Tada</u>, column 3, lines 5 to 17

The Examiner has taken the position that the Tada reference teaches a film thickness of 5 nanometers to 2 microns, preferably 20 nanometers to 2 microns, and most preferably 50 nanometers to 200 nanometers.

In general, the mechanism of photocatalysis is of a surface reaction. The photocatalyst of the Tada reference is not the one proposed in the present application for the following reasons: (A) The photocatalyst disclosed in the Tada reference does not have an advantageous effect on the surfaces of films having increased thicknesses, which leads one to conclude that the photocatalyst is applicable only to the invention of Tada et al., and not applicable to any other examples at all; and (B) the range of film thicknesses is also unique to the invention of Tada et al.

Moreover, the range of film thicknesses proposed in the present application comprises the lower limit in which the film retains its effectiveness and the upper limit in which the film thickness allows the fibers to have the texture of a fabric made of fibers. This range not only takes into consideration productivity and the like but also the adverse effect of having a film thickness that is so thick that it causes the substrate to lose its texture, thereby increasing the hardness of the fabrics that are used for curtains and the like. Accordingly, such hardness also

prevents curtains and the like from being swayed by breeze or from providing similar aesthetic effect.

3. Tada, column 3, lines 18 to 40

The Examiner has taken the position that the Tada reference teaches various deposition methods, stating that it additionally shows deposition upon a substrate and provides substrate forms, such as sheets and fibers.

As discussed above, sputtering has no relevance to the method proposed in the Tada reference. Moreover, the substrate proposed in the Tada reference necessitates the use of an inorganic substrate that withstands baking temperatures. By way of contrast, the organic fibers of the present invention melt or burn at baking temperatures. Hence, the fibers used in the present invention have no relevance to the substrate proposed by the Tada reference.

4. Tada, column 4, lines 41 to 55 and column 6, lines 13 to 15

The Examiner has taken the position that the Tada reference teaches a fiber substrate on which separate photocatalyst and fluorine containing layers are deposited.

The Tada reference targets an inorganic substrate which resists a temperature within the range of $450^{\circ c}$ to $550^{\circ c}$. In contrast, the organic substrate adopted in the present invention melts or burns at these temperatures, and has no relevance to the inorganic substrate used in the Tada reference.

5. Tada, column 3, lines 33 to 45

The Examiner's position is that the Tada reference teaches the light transmittance of the

substrate, stating that the vapor-deposited film would in the absence of unexpected results exhibit the transparency as claimed in the instant invention as titanium oxide is a preferred material and used in overlapping thickness ranges in both the prior-art reference and the instant invention.

The description up to line 49 describes clearly that the substrate in the Tada reference is used for window panes and the like. As a consequence, their substrate is required to have transparency not only to allow light to enter a room, but also to allow light to reach the photocatalyst membrane on the interior side of the substrate.

The intention of the present invention is as follows: the best possible transparency is required of the photocatalyst because, when the photocatalyst membrane is applied to curtains or wallpapers, the patterns on the curtains or wallpapers must be seen without adversely affecting their design performance. Hence, the photocatalyst of the present invention is not relevant to the invention of the Tada reference.

6. Tada, column 4, lines 41 to 45

The Examiner's position is that the Tada reference teaches a fiber cloth.

As previously discussed, the target of the Tada reference is an inorganic substrate which has no relevance to the present invention.

7. Tada, column 7, lines 17 to 20

The Examiner has taken the position that the Tada reference teaches a woven or non-woven cloth substrate.

As previously discussed, the Tada reference targets an inorganic substrate which has no relevance to the present invention.

8. Tada, column 3, lines 31 to 34

The position of the Examiner is that the Tada reference teaches a fibrous substrate.

Descriptions before and after this portion are also related to the argument. This portion can also be interpreted to described an inorganic substrate, which makes this portion irrelevant to the present invention.

9. Tada, column 4, line 44, and column 7, lines 18 to 23

The Examiner's position is that the Tada reference teaches various fibers. But the passages identified by the Examiner describe an inorganic substrate which has no relevance to the present invention.

10. Tada, column 6, lines 35 to 41, and column 17, lines 12 to 18

The Examiner's position is that these two passages from the Tada reference teach oxygen manipulation during the process.

Column 6, lines 35 to 41, describes the mechanism by which the photocatalyst operates. This has no relevance to the present invention.

Column 17, lines 12 to 18, describes the operation of the photocatalyst; this has no relevance to either the production of the photocatalyst membrane or the reasons for rejection.

11. Tada, column 14, lines 47 to 62, and column 16, lines 9 to 23

The Examiner's position is that these two passages from the Tada reference teach vapor deposition.

Column 14, lines 47 to 65, has nothing to do with vapor deposition, which is a vacuum

process. These passages of the Tada reference refer to atmospheric wet processing. The same may be said for column 16, lines 9 to 23.

The Applicants also comment as follows on Comparative Example 5 in column 16 of the Tada reference:

It is impossible to process the organic material of the present invention by the method used in Example 5 because the present organic substrate will not resist such a high temperature or acid. As a result, this example cannot be used as a guideline for processing an organic material.

In addition, as described in the Tada reference, silica film is required in order to prevent impurities (e.g. sodium) contained in the substrate from diffusing into titanium oxide, the photocatalyst. In contrast, the intention of the present invention is to prevent the organic substrate from being decomposed by the photocatalyst. Being organic or inorganic determines the substrate's being decomposed by a photocatalyst or not. Against the similarities in constitutions, the two substrates haven entirely different roles.

Last we lose sight of a real distinction that may be drawn between the teachings of the Tada reference and the present invention, in the present invention a sputtering method is used to deposit a mixture of titanium oxides onto at least one face of an organic (synthetic) fiber substrate. The mixture is obtained by adjusting the amount of oxygen available in the sputtering chamber so that divalent, trivalent and tetravalent oxides of titanium are produced in a mixture. This is neither shown nor suggested in the Tada reference.

In view of the preceding discussion, the Examiner is respectfully requested to accord claims 1 and 3 to 6, as amended above, positive consideration, and to allow them at an early date.

Respectfully submitted,

John F. Gulbin

John F. Gulbin
Registration No. 33,180

212.297.5800
Day Pitney LLP
7 Times Square
New York, NY 10036-7311

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 497 477 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
28.02.2007 Bulletin 2007/09

(21) Application number: **03717459.6**

(22) Date of filing: **25.04.2003**

(51) Int Cl.:
C23C 14/00 (2006.01) *C23C 14/08* (2006.01)
C23C 14/54 (2006.01)

(86) International application number:
PCT/IB2003/001555

(87) International publication number:
WO 2003/091472 (06.11.2003 Gazette 2003/45)

(54) FUNCTIONAL FIBER SHEET

FUNKTIONSFASERFOLIE

FEUILLE DE FIBRES FONCTIONNELLE

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PT RO SE SI SK TR

(30) Priority: **25.04.2002 JP 2002123295**

(43) Date of publication of application:
19.01.2005 Bulletin 2005/03

(73) Proprietor: **Kabushiki Kaisha Suzutora (Suzutora Corporation)**
Gamagori City,
Aichi 443-8623 (JP)

(72) Inventors:
- **Suzuki, Masayuki**
  Gamagori City, Aichi 443-8623 (JP)
- **Nakajima, Eigo**
  Gamagori City,
  Aichi 443-8623 (JP)
- **Suzuki, Toshikazu**
  Gamagori City, Aichi 443-8623 (JP)
- **Suzuki, Takahiro**
  Gamagori City, Aichi 443-8623 (JP)

(74) Representative: **Hoffmann, Jörg Peter**
Müller Hoffmann & Partner
Patentanwälte
Innere Wiener Strasse 17
81667 München (DE)

(56) References cited:
EP-A- 0 507 545
EP-A- 0 886 290
EP-A- 0 957 184
US-A- 4 661 229
US-B1- 6 171 458
US-B1- 6 296 895

- **DATABASE WPI Section PQ, Week 200120 Derwent Publications Ltd., London, GB; Class P27, AN 2001-197174 XP002253889 & JP 2001 017301 A (SUZUTORA SEISEN KOJO KK), 23 January 2001 (2001-01-23)**
- **CANTAO M P ET AL: "Electrochromic behaviour of sputtered titanium oxide thin films" THIN SOLID FILMS, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 259, no. 1, 1 April 1995 (1995-04-01), pages 70-74, XP004004754 ISSN: 0040-6090**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD OF THE INVENTION

[0001] This invention relates to functional fiber sheet coated with physically vapor-deposited film comprising titanium oxide.

RELATED ART

[0002] It is known that by forming metallic or metallic oxide thin film on the surface of fiber sheet comprising synthetic fiber such as woven goods, knit goods, nonwoven fabric, through the use of physical vapor deposition methods such as vacuum vapor deposition, ion beam method, sputtering method, etc., various types of functions can be conferred on the fiber sheet such as electric conductivity, heat-shielding, heat retention, dirt repellency, anti-bacterial properties, deodorizing properties, and the like. However, when the fiber sheet surface is coated with a vapor-deposited film of metal, for example, stainless, titanium, chromium, or copper and the like, color, pattern, etc. on the fiber sheet are hidden by the vapor-deposited film and present a metallic color, lack of variety from a fashion standpoint was a problem. On the one hand, when vapor-deposited film comprising metallic oxides such as titanium oxide, etc. is formed, it was possible to enable color and pattern and the like to become visible by adjusting film thickness so that vapor-deposited film was transparent; on the other hand, there were problems in that electric conductivity was poor in comparison to metallic vapor-deposited film ; heat-shielding properties were inferior as well, moreover, productivity decreased.

[0003] Further, formation of vapor-deposited film is known, having multilayer structure comprising TiO_2 , Ag and TiO_2 as the three layers, vapor-deposited film increasing visible light transmittance while selectively blocking ultraviolet and infrared radiation; however, because this vapor-deposited film peels readily upon repeated washing, it was not practical, moreover, there were problems in that metal oxidized on use, properties deteriorated.

[0004] From EP-A-0 886 290 a decorative resin-made key top coated with a physical vapor-deposited transparent film comprising, for example, TiO_2, TiO or Ti_2O_3 is known.

[0005] Furthermore, US-B1-6 296 895 describes a process for physically vapor-depositing a transparent metal oxide on e.g. a plastic film by controlling the oxidation step and the transparency of the metal oxide film.

[0006] Moreover EP-A-0 507 545 discloses a metal plate coated with a physically vapor-deposited film comprising a mixture of TiO, TiO_2, Ti_2O_3, Ti_3O_5, Ti_nO_{2n-1}, where n is an integer from 4 to 10 and the average oxygen content of the film is from 51 to 59 at%. The resulting film exhibits a bright blue colour.

[0007] This invention, in functional fiber sheet obtained by coating fiber sheet with physically vapor-deposited film, by changing the composition of this physically vapor-deposited film, made the vapor-deposited film transparent so color and pattern on the fiber sheet became visible, furthermore, was able to provide functionality to the vapor-deposited film such as electric conductivity, infrared radiation blocking, ultraviolet radiation blocking and the like, moreover, made productivity increase possible at the time of vapor-deposition.

SUMMARY OF THE INVENTION

[0008] The functional fiber sheet relating to this invention comprises synthetic fiber, one face or both faces thereof being coated with a physically vapor-deposited transparent film comprising metallic oxides, aforementioned metallic oxides characterized as comprising a mixture of ordinary oxides as a main component, containing a small amount of oxides having a lower valence than the ordinary oxides as a secondary component, wherein said metallic oxide is titanium oxide, its ordinary oxide being a tetravalent oxide and said lower valence oxides are divalent or trivalent oxides, and the amount of lower valence oxides to the total amount of the metallic oxides is 0.1 to 20 wt %.

[0009] Synthetic fibers used in this invention comprise thermoplastic synthetic fibers used in usual knit and woven use, exemplified by polyester fiber, nylon fiber, acrylic fiber and polyimide fiber and the like. In particular, polyester fiber is preferred from the standpoint of low moisture content, ease in physical vapor deposition of metals and metallic oxides, and superior durability of the vapor-deposited film. This synthetic fiber can be in either staple or filament form; staple or filament is used without modification in the manufacture of nonwoven fabric, but when used as structural yarn for woven goods or knit goods, filament yarn such as monofilament yarn and multifilament yarn is preferred.

[0010] In this invention, thin film comprisbg metallic oxides comprising titanium oxide is formed on one face or both faces of aforementioned fiber sheet, by physical vapor deposition methods such as vacuum vapor deposition, ion beam method, sputtering method, etc., preferred method is sputtering. Aforementioned metallic oxides comprise ordinary oxide as principal substance, a small amount of oxides having lower valence than the ordinary oxides as a secondary component, hereinafter termed lower oxides is mixed therein. In the oxides of titanium, tetravalent oxide TiO_2 is known as the ordinary oxide, as lower oxides, divalent oxide TiO and trivalent oxide Ti_2O_3 are known. Consequently, the vapor-deposited film of titanium oxide is formed by a mixture of the aforementioned ordinary valence oxides (tetravalent oxides)

and lower valence oxides (divalent or trivalent oxides).

[0011] In physical vapor deposition such as sputtering and the like, while metal is sputter-vaporized in a sealed chamber containing a slight amount of argon gas, it is oxidized by a small amount of oxygen supplied to the chamber, and adsorbed on the fiber sheet, but when the amount of oxygen supplied reaches the amount adequate for production of ordinary oxide, only the ordinary oxide is produced, concurrently, surface of the target metal is oxidized to effect large reduction in the amount of vaporized metal, productivity drops.

[0012] In contrast to this, when the amount of oxygen supplied is an amount less than that needed for production of ordinary oxides, aforementioned lower oxides are also produced concurrently with ordinary oxide, these are adsorbed in the form of mixture on the fiber sheet, moreover, because the target surface is not oxidized, amount of vaporized metal does not decrease, drop in productivity is prevented. Consequently, by forming vapor-deposited film comprising the aforementioned mixture, moreover, by adjusting the thickness of the vapor-deposited film, it becomes possible to provide electric conductivity, heat-shielding, and other functions to the vapor-deposited film while transparency is maintained. Furthermore, in the aforementioned sputtering situation, productivity is improved to an even higher level by admixing a slight amount of nitrogen gas together with argon gas and oxygen.

[0013] In order to set the amount of oxygen supplied at an amount less than that needed for production of ordinary oxide, it is advantageous to determine the unique brightness of light emitted by vaporized metal when the vaporized metal passes through the plasma generated at the time of sputtering, for example, the luminance, and adjust the amount of oxygen supplied so this luminance is maintained at a constant level. When titanium passes through plasma upon sputter vaporization, visible light at wavelength 453 nm is emitted, in the absence of oxygen, the vaporization speed attains a maximum, the brightness is strongest; when excess oxygen is supplied, vaporization speed attains a minimum, brightness decreases as welL Consequently, by adjusting the amount of oxygen supplied on the basis of luminance, it becomes possible to control the amount of lower oxide. Further, it is possible to use any desired intensity index correlated to luminance, instead of luminance itself.

[0014] Mixture content of oxides having valence lower than that of aforementioned ordinary oxide, in other words, lower oxide, is 0.1 to 20 wt% of the total oxides; when this mixture content is less than 0.1 wt%, functions such as electric conductivity and heat-shielding are not obtained, moreover, productivity is drastically decreased; in contrast, at more than 20 wt%, metallic color is evident, moreover, visible light transmittance is insufficient, fiber sheet attributes are lost. Further, thickness of the aforementioned physically vapor-deposited film is preferably 5~ 500 nm, in particular, 30 ~ 300 nm; at less than 5 mn, functions such as electric conductivity, heat-shielding, infrared radiation cuts, ultraviolet radiation cuts, etc. are not obtained, at greater than 500 nm, structural fibers, color, pattern, etc. of the fiber sheet are not visible, there are difficulties in attaining practical use from a cost standpoint as well.

[0015] Further, transparency of the aforementioned physically vapor-deposited film is preferably 30% or more for visible light transmittance at wavelength 550 nm, at less than 30%, color and pattern on the surface of the fiber sheet [and] fibers are no longer visible, fiber sheet attributes are lost. Further, transmittance of infrared radiation and ultraviolet radiation is fixed by the mixture content of the lower valence oxides, but when infrared radiation cuts comprise the objective, it is preferable to set the mixture content on the high side and suppress the infrared radiation transmittance to 70% or less at wavelength 1000 nm. Further, when ultraviolet radiation cuts comprise the objective, it is preferable to set the aforementioned mixture content on the low side and suppress the ultraviolet radiation transmittance to 50% or less at wavelength 400 nm.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016]

Figure 1 is a cross-sectional diagram of sputtering device related to Working Example 1.
Figure 2 is a graph showing light transmittance of vapor-deposited film.
Figure 3 is a graph showing light reflectivity of vapor-deposited film.

DETAILED DESCRIPTION OF THE INVENTION

EXAMPLES OF THE INVENTION

Example 1

[0017] As fiber sheet, woven fabric using polyester fiber multifilament yam as warp and weft is used, transparent coating of titanium oxide is formed on its surface by sputtering, having thickness of 5 - 500 nm, preferably 30 ~ 300 nm.

[0018] Figure 1 shows one example of a sputtering device, sealable chamber 10 is divided by horizontal divider 11 into sputtering chamber 12 below and fabric chamber 13 above, in the middle of sputtering chamber 12 below, flat plate

target 14 comprising titanium is fixed on target source 15 located in mid-air, target 14 is cooled from its bottom face by cold water passing through this target source 15. Anode 16 is affixed horizontally at the left and right above this target 14, direct current voltage of 200 ~ 1000 V is impressed by means of direct current power source 17 between this anode 16 and target 14.

[0019] Water-cooled cylinder 18 is affixed horizontally above aforementioned anode 13 , and moreover, rotates freely, above this to the left, fiber sheet sending shaft 19, further, above and to the right, fiber sheet F winding shaft 20 are respectively horizontally affixed, moreover, these rotate freely. Thus, pre-process fiber sheet F wrapped around sending shaft 19 is pulled out, wrapped around aforementioned water-cooled cylinder 18 through guide roller 21 at upper left, and wound on winding shaft 20 through guide roller 22 at upper right. Further, vacuum pump 23, argon gas supply gas bomb 24, and oxygen gas supply gas bomb 25 are respectively connected to aforementioned chamber 10.

[0020] In the aforementioned device, sending shaft 19, winding shaft 20, and water-cooled cylinder 18 are rotated, fabric F is sent at a fixed speed in counterclockwise direction while being cooled on water-cooled cylinder 14, surface temperature of fabric F is maintained at 60°C or lower. On the other hand, vacuum pump 23 is driven to reduce internal pressure in chamber 10 to about 1.3×10^{-3} Pa, next, argon gas from argon gas supply gas bomb 24 and oxygen from oxygen gas supply gas bomb 25 are respectively introduced to adjust the internal pressure of chamber 10 to about 1×10^{-2} Pa, sputtering is implemented thereafter, titanium emitted from target 14 is reacted with oxygen to form titanium oxide, this is allowed to adhere on aforementioned fiber sheet F, transparent physically vapor-deposited film is formed.

[0021] At this time, sputtering is implemented while brightness of vaporized titanium passing through plasma above target 14 is observed; during this time, by adjusting the amount of oxygen sent from oxygen gas supply gas bomb 25 to chamber 10, the luminance of aforementioned vaporized titanium or any desired intensity index correlated to luminance is controlled at a fixed level determined by tests beforehand; by this means titanium oxide comprises [a mixture of] ordinary oxides and lower oxides, the mixture is formed wherein the amount of lower oxide to the total amount of metallic oxides is 0.1 ~ 20 wt%, to be adsorbed on fiber sheet F. Further, traveling speed of fiber sheet F is adjusted so that physically vapor-deposited film comprising aforementioned titanium oxide has thickness of 5 - 500 nm.

[0022] In the aforementioned Working Example, as the amount of oxygen supplied to chamber 10 is set higher, further, as the setting for luminance is set lower, there is increase in ordinary oxide and decrease in lower oxide, transparency of the physically vapor-deposited film increases. On the other hand, as the amount of oxygen supplied is set lower, further, as the setting for luminance (intensity) is set higher, there is decrease in ordinary oxide and increase in lower oxide, transparency of the physically vapor-deposited film decreases, metallic color becomes stronger. Furthermore, by the aforementioned adjustment of luminance, it becomes possible to maintain visible light transmittance at 20% or more, while infrared radiation transmittance or ultraviolet radiation transmittance is suppressed at 70% or less.

[0023] By using warp-knit fabric comprising polyester fiber multifilament yarn as the aforementioned fiber sheet, and other than that, implementing sputtering just as described above, fiber sheet was obtained that had electric conductivity and heat-shielding properties, moreover, was provided with the attributes of warp-knit fabric, had visible light transmittance of 30% or more, infrared radiation transmittance or ultraviolet radiation transmittance of 70% or less.

[0024] Further, by using spun-bonded nonwoven fabric comprising polyester filament as the aforementioned fiber sheet, and other than that, implementing sputtering just as described above, fiber sheet was obtained that had electric conductivity and heat-shielding properties, moreover, was provided with the attributes of spun-bonded nonwoven fabric, had visible light transmittance of 30% or more, infrared radiation transmittance or ultraviolet radiation transmittance of 70% or less.

Example 2

[0025] By using sputtering device in Figure 1, implementing sputtering on one face of fiber sheet comprising woven goods, knit goods or nonwoven fabric, etc., to form aforementioned physically vapor-deposited film, thereafter removing aforementioned fiber sheet temporarily, thereafter reversing the front and back and reattaching to the sputtering device, thereafter implementing sputtering on the other face identically as aforementioned, fiber sheet is obtained, having aforementioned physically vapor-deposited film on both front and back faces, having visible light transmittance of 30% or more, infrared radiation transmittance or ultraviolet radiation transmittance of 70% or less, moreover, being provided with attributes of fiber sheet, color and pattern being visible thereon, having no metallic color.

Example 3

[0026] In the aforementioned sealed chamber, 2 sets of vapor deposition devices are set up in rows, sputtering is implemented continuously on both front and back faces to form the aforementioned physically vapor-deposited film. For example, No. 1 water-cooled cylinder and No. 2 water-cooled cylinder are set up in parallel to the left and right of center in the sealed chamber, No. 1 water-cooled cylinder on the left is rotated in counterclockwise direction, No. 2 water-cooled cylinder on the right is rotated in clockwise direction, respectively; sputtering is implemented by wrapping fiber

sheet from the left so that its back face comes in contact with the lower half of No. 1 water-cooled cylinder, next, [sheet is] led to top right of No. 2 water-cooled cylinder, sputtering is implemented by wrapping fiber sheet from the right so that its front face comes in contact with the lower half of this No. 2 water-cooled cylinder.

[0027] As fiber sheet F in Working Example 1, 190-count taffeta using polyester multifilament yarn in warp and weft was used, transparent physically vapor-deposited film of titanium oxide was formed on one face thereof by sputtering. As oxygen supply control, "Dual Magnetron Cathode Plasma Emission Monitor" ("von Alden", Germany) was used; monochromatic light (wavelength 453 nm) unique to metallic titanium was taken out with collimator to determine luminance, aforementioned luminance was expressed as intensity, where luminance at zero oxygen supply was 100, luminance at excess oxygen supply was 10; Test Sample A was obtained when this intensity was set at 50. Also, Test Sample B was obtained when intensity was set at 30.

[0028] The compositions of physically vapor-deposited film for Test Sample A and Test Sample B were analyzed by X-ray photoelectron spectrophotometry. As the analytical device, SSX-100 Model X-ray Photoelectron Spectrophotometer (SSI Co.) was used. Upon analysis by using monochromatic A1Kα (100W) as the x-ray source, in Test Sample A at intensity 50, about 5% trivalent lower oxide Ti_2O_3 was also present in tetravalent ordinary oxide. Further, in Test Sample B at intensity 30, this vapor-deposited film was formed almost completely with tetravalent ordinary oxide TiO_2. Ratio of titanium and oxygen in the vapor-deposited film was 1/2.15 in Test Sample A, 1/2.39 in Test Sample B. Further, external appearances were compared for the aforementioned Test Sample A and B, the results, together with the aforementioned analytical results are shown in Table 1 below.

Table 1

	Test Sample A	Test Sample B
Intensity	50	30
Thickness of vapor-deposited film (μm)	50	50
External appearance	Colorless transparent	Colorless transparent
Titanium/oxygen (atom ratio)	1/2.15	1 / 2.39
Low valence oxide content	5%	0%

[0029] Vapor-deposited film of aforementioned titanium oxide was formed on transparent film having thickness of 50 μm, comprising polyethylene terephthalate, to measure the electric conductivity and light transmittance of the aforementioned vapor-deposited film. At this time, Test Samples 1~6 were prepared by changing intensity in 6 steps, 70, 60, 50, 40, 30, 20. Then electric conductivity, light transmittance at wavelength 400 ~ 1000 nm and light reflectivity were respectively measured for these Test Samples 1~6. Electric conductivity is shown in Table 2, light transmittance in Figure 2, light reflectivity in Figure 3, respectively.

Table 2

Test Sample No.	1	2	3	4	5	6
Intensity	70	60	50	40	30	20
Electric conductivity (Ω/cm)	8×10^3	1×10^4	7×10^4	4×10^7	-	-

[0030] As shown in aforementioned Table 2, when electric conductivity is compared in terms of resistance values, Test Sample 1 having intensity 70, containing the most lower oxide, has the lowest resistance value; as the amount of lower oxide decreases, resistance values decrease in the order of Test Sample 2 having intensity 60, Test Sample 3 having intensity 50, Test Sample 4 having intensity 40; resistance values could not be measured for Test Sample 5 having intensity 30 and Test Sample 6 having intensity 20, electric conductivity was essentially zero.

[0031] Further, in light transmittance, as shown in Figure 2, Test Sample 4~6 having low intensity had high transmittance, transparency increased, in contrast, in Test Sample 1~3 having high intensity, transmittance decreased, there was a tendency for external appearance to present a metallic color. Further, in Test Sample 6 having intensity 20, transmittance was 60 % or more in the entire range including ultraviolet radiation to infrared radiation, from wavelength 400 nm to 1000 nm. In Test Sample 5 having intensity 30, ultraviolet radiation transmittance at wavelength 400 nm was less than 50 %, but for the remaining visible light and infrared radiation, transmittance was 50 ~ 70 %. In Test Sample 4 having intensity 40, infrared radiation transmittance was lower than 70 %, although tendency somewhat similar to Test Sample 3 was displayed.

[0032] Further, in Test Sample 3 having intensity 50, visible light transmittance at wavelength 550 nm was about 50 %, for ultraviolet radiation at wavelength 400 nm, about 45 %, for infrared radiation at wavelength 1000 nm, about 43

%. Further, in Test Sample 2 having intensity 60, about equal transmittance was observed in the range of 40~45 % from ultraviolet radiation at wavelength 400 nm to visible light at wavelength 700 nm; transmittance gradually decreased beyond 700 nm, and was about 35 % at infrared radiation wavelength 1000 nm. Further, in Test Sample 1 having intensity 70, transmittance decreases gradually from about 37 % to 30 %, from ultraviolet radiation at wavelength 400 to infrared radiation at wavelength 1000 nm, Furthermore, light transmittance of the aforementioned film itself was about 85 % at wavelength 400 nm, about 88 % at wavelength 550 nm, about 89 % at wavelength 1000 nm; there was a very slight upward trend to the right.

[0033] On the other hand, light reflectivity, as shown in Figure 3, had a somewhat downward slope to the right in Test Sample 4~6 having low intensity, in Test Sample 1~3 having high intensity, a tendency toward a somewhat upward slope to the right was observed. However, Test Sample 6 having intensity 20 showed the highest reflectivity of about 28 % at wavelength 500 - 600 nm in the visible light range, there was a sudden drop on the ultraviolet radiation side, a gradual decrease on the infrared radiation side, the curve had a mountain shape. Also, in Test Sample 5 having intensity 30 and Test Sample 4 having intensity 40, the downward slopes to the right were more or less similar, reflectivity at wavelength 400 nm was about 33 %, reflectivity at wavelength 1000 nm was 17 ~ 19 %.

[0034] Further, Test Sample 3 having intensity 50 showed the lowest reflectivity of about 19 % at wavelength 500 - 600 [nm] in the visible light range, there was a gradual increase toward wavelength 400 nm and 1000 nm to about 22 - 23 %. Further, Test Sample 2 having intensity 60 showed more or less uniform reflectivity of 16~ 17 % at wavelength 550 nm or less, there was a gradual increase to reflectivity of 26 % at wavelength 1000 nm. Further, in Test Sample 1 having intensity 70, reflectivity increased more or less linearly following the wavelength, to about 18 % at wavelength 400 nm, about 37 % at wavelength 1000 nm. Furthermore, reflectivity of the film itself showed a constant value of some 11 % in the entire wavelength range of 400 - 1000 nm.

[0035] As described above, because in functional fiber sheet relating to this invention, metallic oxides constituting its physically vapor-deposited film comprise not only ordinary oxide but also contain a small amount of lower oxide, by setting the amount of lower oxide in the amount of mixture, it is possible to maintain transparency of the vapor-deposited film so color and pattern of the fiber sheet are visible, fashionability and attributes of the fiber sheet are maintained, at the same time, functionality is provided such as electric conductivity, heat-shielding, infrared radiation blocking, ultraviolet radiation blocking, dirt repellency, anti-bacterial properties and corrosion resistance and the like, by means of the vapor-deposited film; moreover, productivity is satisfactory, and there is superior washability and peel resistance. Consequently, the aforementioned functional fiber sheet is very suitable for uses such as industrial materials, e.g. mesh screen and filter and the like, insect netting, house-wrapping material, also, outdoor tent, umbrella, indoor decorative wall panel material, ceiling material, and interior material and the like, having superior corrosion resistance and washability as well, being able to satisfy fashionability and various functionalities.

[0036] While three examples of the present invention has been shown and described, it is to be understood that many changes and modifications may be made thereunto without departing from the scope of the invention as defined in the appended claims.

Claims

1. A functional fiber sheet comprising synthetic fiber, one face or both faces thereof being coated with a physically vapor-deposited transparent film comprising metallic oxides, wherein said metallic oxides comprise a mixture of an ordinary oxide as a main component and a small amount of oxides having a lower valence than the ordinary oxide as a secondary component, wherein said metallic oxide is titanium oxide, its ordinary oxide being a tetravalent oxide and said lower valence oxides are divalent or trivalent oxides, and the amount of lower valence oxides to the total amount of the metallic oxides is 0.1 to 20 wt %.

2. The functional fiber sheet as set forth in Claim 1 wherein the thickness of said physically vapor-deposited film is 5 to 500 nm.

3. A method for manufacturing a functional fiber sheet comprising the steps of : forming a physically vapor-deposited transparent film of metallic oxides on a fiber sheet through a physical vapor deposition process; forming an ordinary oxide as a main component of the metallic oxides of the physically vapor-deposited film by increasing the amount of oxygen to be supplied during the physical vapor deposition process; and forming a small amount of oxides having a lower valence than the ordinary oxides as a secondary component of the metallic oxides by lowering the amount of oxygen to be supplied to the physical vapor deposition process, wherein said metallic oxide is titanium oxide, its ordinary oxide being a tetravalent oxide and said lower valence oxides are divalent or trivalent oxides and the amount of lower valence oxides to the total amount of the metallic oxides is 0.1 to 20 wt %.

4. The functional fiber sheet as set forth in Claim 1 wherein the synthetic fiber comprises synthetic fiber used in usual knit and woven use.

5. The functional fiber sheet as set forth in Claim 1 wherein the synthetic fiber comprises polyester fiber, nylon fiber, acrylic fiber or polyimide fiber.

Patentansprüche

1. Funktionsfaserfolie umfassend eine synthetische Faser, wobei eine oder beide Flächen davon mit einem physikalisch dampfabgeschiedenen transparenten Film, umfassend Metalloxide, beschichtet sind, worin die Metalloxide eine Mischung eines normalen Oxids als eine Hauptkomponente und eine geringe Menge von Oxiden mit einer niedrigeren Wertigkeit als das normale Oxid als eine sekundäre Komponente umfassen, wobei das Metalloxid Titanoxid darstellt, dessen normales Oxid ein vierwertiges Oxid darstellt und dessen Oxide mit niedrigerer Wertigkeit die zweiwertigen oder dreiwertigen Oxide darstellen, und die Menge an Oxiden mit niedrigerer Wertigkeit, bezogen auf die Gesamtmenge der Metalloxide, 0,1 bis 20 Gew.-% beträgt.

2. Funktionsfaserfolie nach Anspruch 1, worin die Dicke des physikalisch dampfabgeschiedenen Films 5 bis 500 nm beträgt.

3. Verfahren zur Herstellung einer Funktionsfaserfolie, umfassend die Schritte: Bilden eines physikalisch dampfabgeschiedenen transparenten Films von Metalloxiden auf einer Faserfolie durch ein physikalisches Dampfabscheidungsverfahren; Bilden eines normalen Oxids als einer Hauptkomponente der Metalloxide des physikalisch dampfabgeschiedenen Films durch Erhöhen der Menge an Sauerstoff, die während des physikalischen Dampfabscheidungsverfahrens zugeführt wird; und Bilden einer geringen Menge von Oxiden mit niedrigerer Wertigkeit als den normalen Oxiden als eine sekundäre Komponente der metallischen Oxide durch Verringern der Menge an Sauerstoff, die während des physikalischen Dampfabscheidungsverfahrens zugeführt wird, wobei das Metalloxid Titanoxid darstellt, dessen normales Oxid ein vierwertiges Oxid darstellt und dessen Oxide mit niedrigerer Wertigkeit die zweiwertigen oder dreiwertigen Oxide darstellen, und die Menge an Oxiden mit niedrigerer Wertigkeit, bezogen auf die Gesamtmenge der Metalloxide, 0,1 bis 20 Gew.-% beträgt.

4. Funktionsfaserfolie nach Anspruch 1, worin die synthetische Faser synthetische Fasern umfasst, die in üblichen Wirk- und Webanwendungen eingesetzt werden.

5. Funktionsfaserfolie nach Anspruch 1, worin die synthetische Faser Polyesterfasern, Nylonfasern, Acrylfasern oder Polyimidfasern umfasst.

Revendications

1. Nappe de fibres fonctionnelle comprenant des fibres synthétiques, dont l'une au moins des deux surfaces est revêtue d'un film transparent appliqué par dépôt physique en phase vapeur et comprenant des oxydes métalliques, lesdits oxydes métalliques comprenant un mélange d'un oxyde ordinaire comme composant principal et d'une faible quantité d'oxydes ayant une valence inférieure à celle de l'oxyde ordinaire comme composant secondaire, dans laquelle ledit oxyde métallique est l'oxyde de titane, son oxyde ordinaire étant un oxyde tétravalent, et lesdits oxydes de valence inférieure sont des oxydes divalents ou trivalents, la quantité d'oxydes de valence inférieure par rapport à la quantité totale des oxydes métalliques étant de 0,1 à 20 % en poids.

2. Nappe de fibres fonctionnelle selon la revendication 1, dans laquelle l'épaisseur dudit film appliqué par dépôt physique en phase vapeur est de 5 à 500 nm.

3. Procédé de fabrication d'une nappe de fibres fonctionnelle, comprenant les étapes consistant à : former un film transparent d'oxydes métalliques appliqué par dépôt physique en phase vapeur sur une nappe de fibres par un procédé de dépôt physique en phase vapeur ; former un oxyde ordinaire comme composant principal des oxydes métalliques du film appliqué par dépôt physique en phase vapeur en augmentant la quantité d'oxygène devant être fournie au cours du procédé de dépôt physique en phase vapeur ; et former une faible quantité d'oxydes ayant une valence inférieure à celle des oxydes ordinaires comme composant secondaire des oxydes métalliques en diminuant la quantité d'oxygène devant être fournie au procédé de dépôt physique en phase vapeur, dans lequel ledit oxyde

métallique est l'oxyde de titane, son oxyde ordinaire étant un oxyde tétravalent, et lesdits oxydes de valence inférieure sont des oxydes divalents ou trivalents, la quantité d'oxydes de valence inférieure par rapport à la quantité totale des oxydes métalliques étant de 0,1 à 20 % en poids.

4. Nappe de fibres fonctionnelle selon la revendication 1, dans laquelle les fibres synthétiques comprennent les fibres synthétiques utilisées dans des processus de tricotage et de tissage usuels.

5. Nappe de fibres fonctionnelle selon la revendication 1, dans laquelle les fibres synthétiques comprennent les fibres polyester, les fibres de nylon, les fibres acryliques ou les fibres de polyimide.

FIG 1

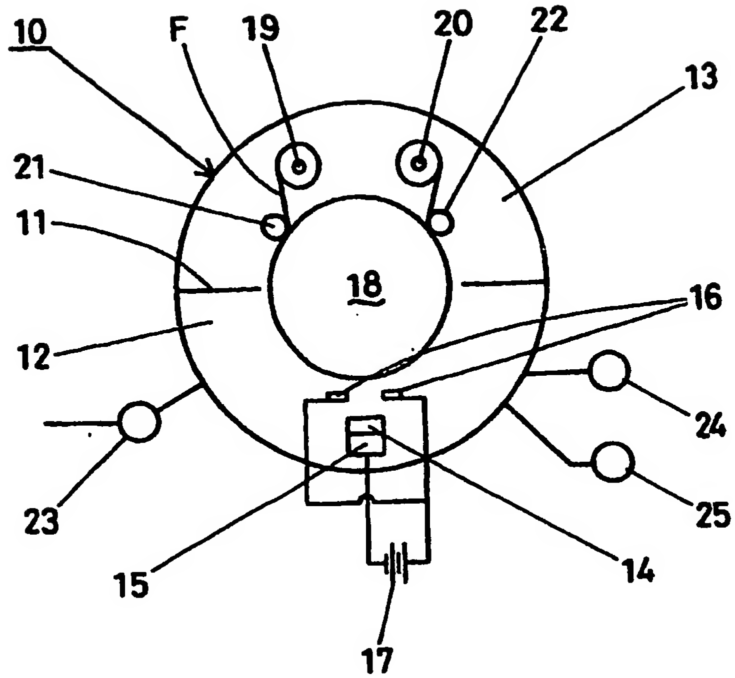
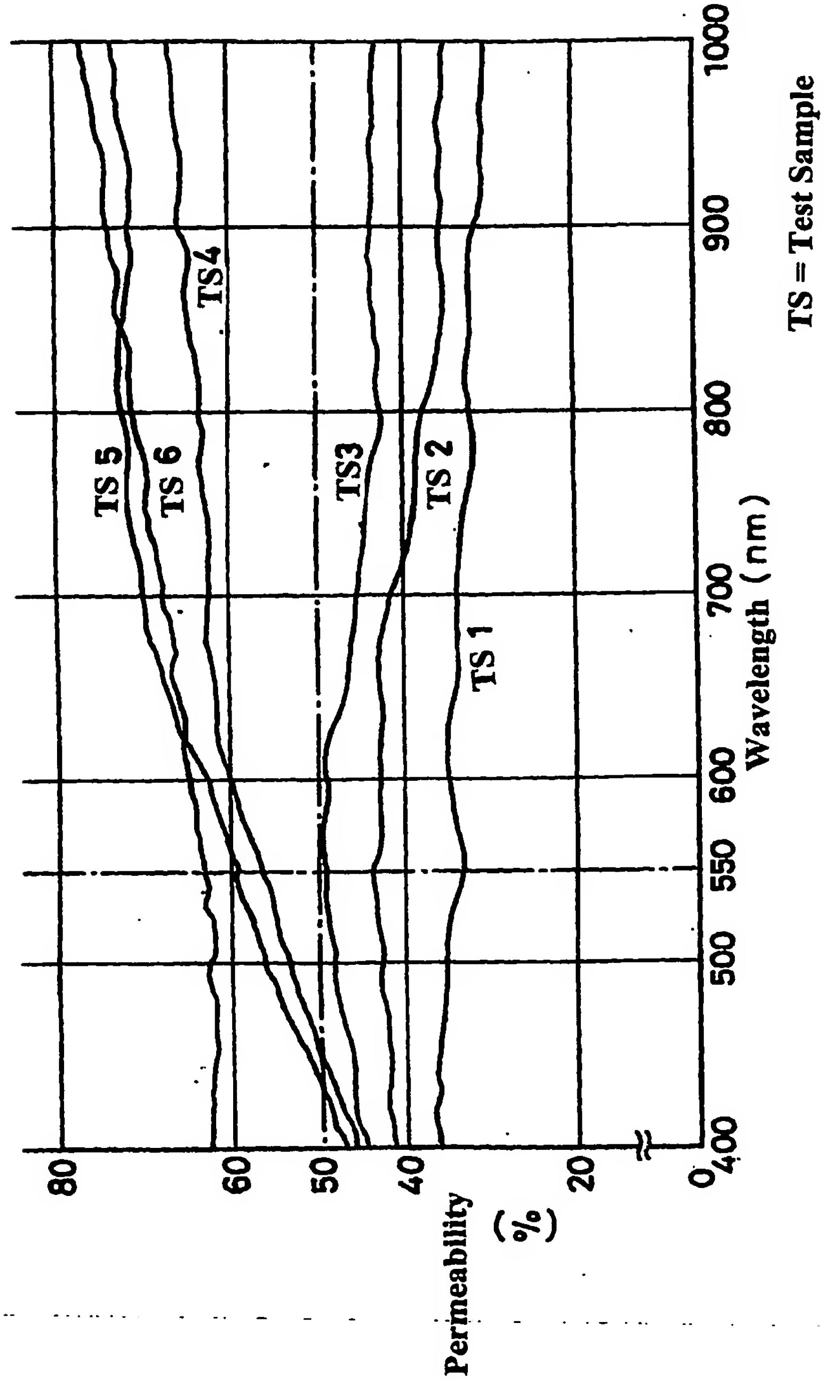
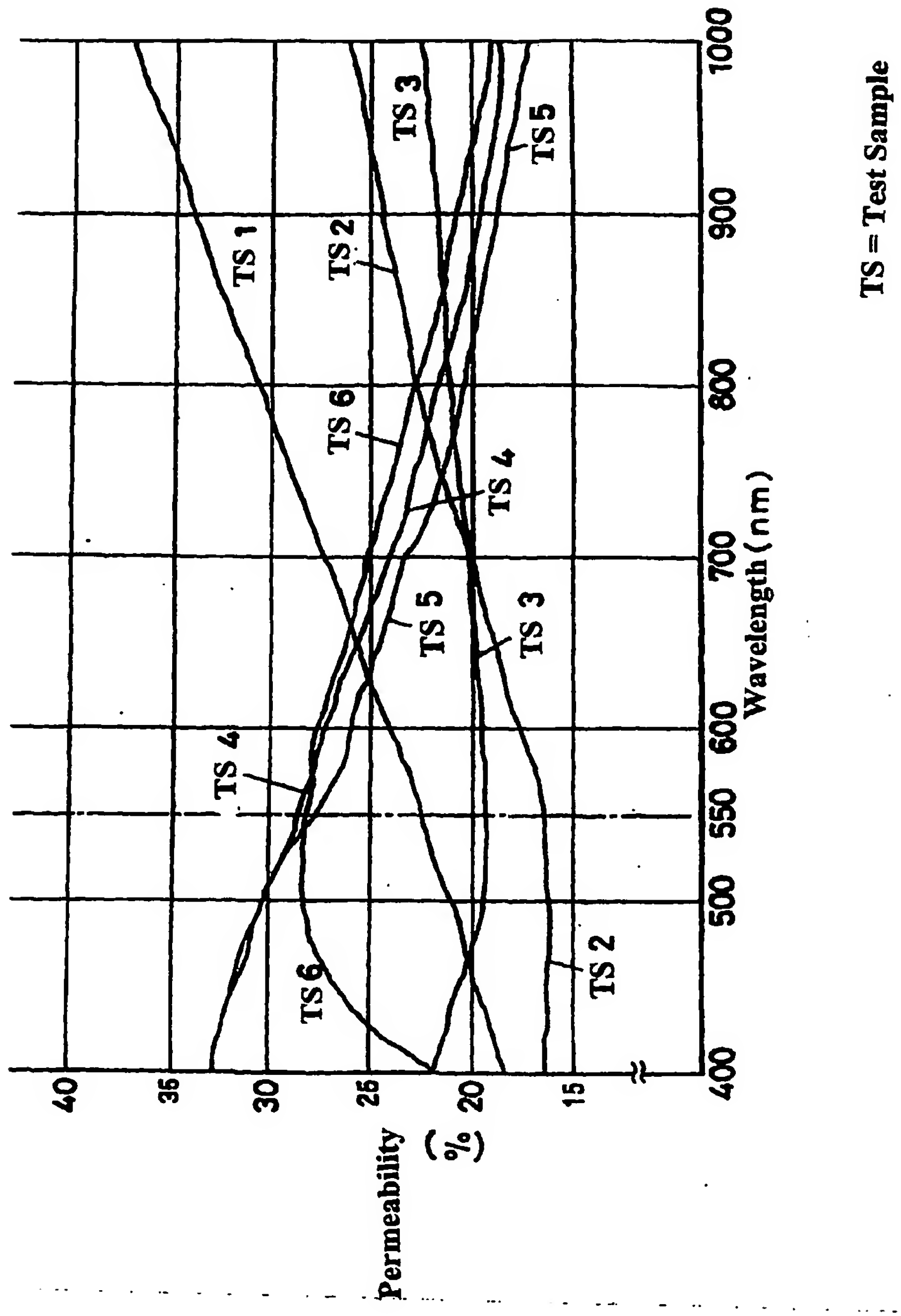


FIG 2



Permeability (%)
80
60
50
40
20
0
400
500
550
600
700
800
900
1000
Wavelength (nm)
TS 1
TS 2
TS3
TS4
TS 5
TS 6
TS = Test Sample

FIG 3


Permeability (%)
40
35
30
25
20
15
400
500
550
600
700
800
900
1000
Wavelength (nm)
TS 1
TS 2
TS 3
TS 4
TS 5
TS 6
TS = Test Sample